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# Interaction of Hydrogen and Hydrocarbons with Transition Metals. Neutron Diffraction Study of the Crystal and Molecular Structure of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$)

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The crystal and molecular structure of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$) has been determined by using single-crystal neutron diffraction. The complex crystallizes in the orthorhombic space group $Pn2_1a$ with lattice parameters at 110 K of $a$ = 18.502 (9), $b$ = 10.096 (5), and $c$ = 8.763 (4) Å. The molecule consists of a triangular array of Os atoms with one nonbridged edge (Os–Os = 2.855 (3) Å), one edge bridged by a single hydride (Os–Os = 3.053 (3) Å), and a third edge doubly bridged by a hydride atom and a methylene ligand (Os–Os = 2.824 (3) Å). The complex contains no terminal hydride ligands. The methylene carbon atom has a distorted tetrahedral geometry with an Os–C–Os angle of 82.1 (1)° and a H–C–H angle of 106.0 (8)°.

## Introduction

The reaction between diazomethane and ($\mu$-H)$_2$Os$_3$(CO)$_{10}$, the neutron diffraction structure of which is presented in the preceding paper in this issue,[2] yields a product for which the two tautomers ($\mu$-H)Os$_3$(CO)$_{10}$($\mu$-CH$_3$) and ($\mu$-H)$_2$Os$_3$-(CO)$_{10}$($\mu$-CH$_2$) exist in equilibrium in solution, based on variable-temperature $^1$H and $^{13}$C NMR evidence.[3] This was the first direct observation of the interconversion between methyl and methylene ligands. We have previously reported[4] the neutron diffraction structure of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$) using a crystal obtained from the reaction of CH$_2$N$_2$ with fully deuterated ($\mu$-D)$_2$Os$_3$(CO)$_{10}$, in which the H/D isotope distribution among the four hydrogen atomic sites was determined. These studies are of particular interest because of the possible relevance of metal cluster complexes as models for catalytically active metal surfaces.[5]

In the neutron diffraction study of partially deuterated ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$),[4] the small size of the crystal coupled with a scattering cancellation from certain hydrogen sites due to a specific H/D isotope ratio resulted in a somewhat imprecise determination of certain hydrogen positions. In fact, the location of one of the hydride ligands could only be inferred from the geometry of the rest of the molecule. A high-precision structural study of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$) is important for at least three reasons: (1) Metal–carbene complexes have been postulated as intermediates in many catalytic reaction sequences.[6] Since only two other complexes with bridging methylene ligands have been structurally characterized,[7,8] additional structural data is required in order to provide a better understanding of their structure and bonding. (2) We are afforded the opportunity of comparing the structural parameters of two different bridging hydrido ligands in the same cluster complex. (3) We can accurately compare

the neutron diffraction structure of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$) to that of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$[2] and determine which bonding models, if any, correctly predict their geometries. Since we were fortunate in growing large crystals which are fully protonated, we report the results of a single-crystal neutron diffraction study of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$($\mu$-CH$_2$) herein.

## Experimental Section

**Neutron Data Collection.** The reaction of ($\mu$-H)$_2$Os$_3$(CO)$_{10}$ and CH$_2$N$_2$ in methylene chloride slowly yields crystals of the less soluble methylene tautomer at −2 °C.[3] A crystal of the title compound having dimensions 2.1 × 2.1 × 0.9 mm and weighing 14 mg was selected and sealed in a lead-glass capillary. With the crystal mounted in an arbitrary orientation and cooled to ~110 K with a nitrogen cold stream,[9,10] all neutron diffraction data were collected using the computer-controlled diffractometer at the CP-5 reactor at Argonne National Laboratory. The unit cell dimensions (see Table I) were obtained from a least-squares refinement of the angular settings of 14 automatically centered reflections (40° ≤ 2$\theta$ ≤ 60°).

One octant ($+h$, $+k$, $+l$) of neutron data was measured out to (sin $\theta$)/$\lambda$ = 0.62 Å$^{-1}$ using the $\theta$–2$\theta$ step–scan mode with 0.1° steps. The instrumentation and data collection techique have been described elsewhere.[11] A set of $F_o{}^2$ values, where $F_o$ is the observed structure factor amplitude, was obtained by applying Lorentz and absorption corrections to the data.[12] Reflections with net intensities less than zero were assigned $F_o{}^2$ values of zero. The variance of each $F_o{}^2$ was calculated from standard counting statistics with an added factor of $(0.05F_o{}^2)^2$ based on the 5% maximum variation of two reference reflections which were measured periodically throughout the data collection.

**Solution and Refinement of the Structure.** Initial nonhydrogen atom positional coordinates were obtained from the neutron structural solution of the partially deuterated compound.[4] The four hydrogen atoms were located on a Fourier map with phases determined from the refined coordinates of the nonhydrogen atoms. In the final stages of least-squares refinement,[13,14] the data were corrected for secondary
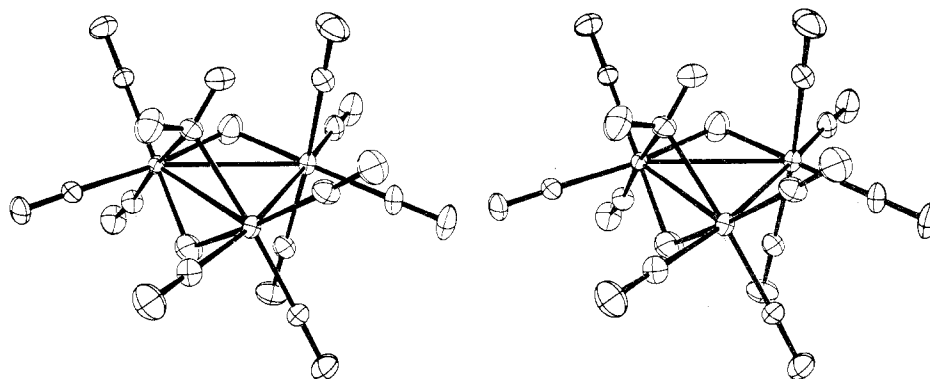
**Figure 1.** Stereoscopic view of the $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ molecule. Thermal ellipsoids are scaled to 50% probability. The atom labeling scheme is given in Figures 2 and 3.

**Table I.** Crystal and Experimental Data for the Neutron Diffraction Study of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$

(A) Crystal Parameters at 110 K

crystal class: orthorhombic    $V = 1637$ (1) Å³
space group: $Pn2_1a^a$    $Z = 4$
$a = 18.502$ (9) Å    mol wt 866.8
$b = 10.096$ (5) Å    $\rho$(calcd) = 3.517 g cm⁻³
$c = 8.763$ (4) Å

(B) Data and Refinement Parameters

neutron wavelength: 1.142 (1) Å
$\mu$(calcd) = 0.61 cm⁻¹
range of transmission coeffs: 0.89–0.95
refined isotropic extinction coeff, $g$: 0.17 (3) × 10⁻⁴
range of extinction correction factors: 1.00–1.29
standard dev of an observn of unit weight: 0.938
no. of independent data: 1548
$R(F_o) = 0.074$
$R(F_o^2) = 0.077$
$R_w(F_o^2) = 0.100$

$^a$ Nonstandard setting of space group $Pna2_1$ $[C_{2v}^9;$ No. 33].

extinction[15] and the thermal motion of all of the atoms was treated anisotropically. The final discrepancy indices are given in Table I and the positional and thermal parameters from the final least-squares

cycle are presented in Table II. A scaled difference Fourier map based on the final refined parameters was featureless.

## Results and Discussion

The molecular structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$, shown in Figure 1, consists of a triangular array of three osmium atoms each of which has a distorted octahedral coordination geometry if the direct Os(1)–Os(2) and Os(1)–Os(3) vectors are not considered. The edges of the $Os_3$ triangle have no bridging ligands (Os(2)–Os(3) = 2.855 (2) Å), a bridging hydride (Os(1)–Os(3) = 3.053 (3) Å), or a bridging hydride and methylene (Os(1)–Os(2) = 2.824 (3) Å). Thus, the monobridged edge is 0.198 (3) Å longer than the nonbridged edge, while the doubly bridged edge is 0.031 (3) Å shorter. This type of metal–metal bond length variation has been reported by Churchill and co-workers in structural studies of other $Os_3^{16}$ and $Ru_3^{17}$ triangular clusters. The four-atom $Os_2(\mu\text{-C})(\mu\text{-H})$ moiety is nonplanar, with a dihedral angle of 154.0 (5)° between the Os(1)–C(11)–H(4) and Os(2)–C(11)–H(4) planes (see Table V). The closest intermolecular contacts are H(1)⋯H(4) = 2.084 (14), H(2)⋯H(4) = 2.742 (14), H(1)⋯O(10) = 3.005 (12) Å, and a number of O⋯O distances of ~3.05 Å. Therefore, the molecular packing is assumed to be primarily dictated by van der Waals forces.

**Table II.** Final Positional$^a$ and Thermal$^b$ Parameters for $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$

| ATOM | X | Y | Z | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|---|---|---|
| OS1 | -0.0095(1) | 0.25 | 0.2145(2) | 0.0116(9) | 0.018(1) | 0.015(1) | -0.001(1) | 0.0001(8) | 0.003(1) |
| OS2 | 0.0955(1) | 0.2490(5) | -0.0195(2) | 0.0133(9) | 0.017(1) | 0.015(1) | 0.000(1) | 0.0019(8) | -0.004(1) |
| OS3 | 0.1523(1) | 0.2517(5) | 0.2834(2) | 0.0127(9) | 0.021(1) | 0.016(1) | -0.001(1) | 0.000(1) | -0.002(2) |
| C1 | -0.0928(2) | 0.2659(6) | 0.0909(4) | 0.018(2) | 0.019(2) | 0.021(2) | 0.002(2) | -0.000(1) | 0.002(2) |
| O1 | -0.1417(2) | 0.2747(7) | 0.0116(6) | 0.020(2) | 0.030(3) | 0.032(2) | -0.002(2) | -0.013(2) | 0.001(3) |
| C2 | -0.0545(2) | 0.1214(6) | 0.3434(6) | 0.018(2) | 0.024(2) | 0.021(2) | -0.000(2) | 0.002(2) | 0.007(2) |
| O2 | -0.0824(3) | 0.0412(8) | 0.4117(8) | 0.033(3) | 0.032(3) | 0.033(3) | -0.008(3) | 0.003(3) | 0.012(3) |
| C3 | -0.0365(3) | 0.4043(6) | 0.3353(6) | 0.023(2) | 0.020(2) | 0.023(2) | 0.001(2) | -0.000(2) | -0.005(2) |
| O3 | -0.0593(2) | 0.4906(7) | 0.4075(8) | 0.032(3) | 0.026(3) | 0.039(3) | 0.004(3) | 0.002(3) | -0.013(3) |
| C4 | 0.0386(2) | 0.2575(7) | -0.2019(4) | 0.022(2) | 0.025(2) | 0.016(2) | 0.000(2) | -0.001(1) | -0.004(3) |
| O4 | 0.0042(3) | 0.2646(10) | -0.3081(5) | 0.038(2) | 0.043(3) | 0.026(2) | 0.005(4) | -0.010(2) | -0.003(4) |
| C5 | 0.1627(3) | 0.1220(6) | -0.0946(6) | 0.028(2) | 0.020(2) | 0.021(2) | 0.005(2) | 0.001(2) | 0.000(2) |
| O5 | 0.2019(3) | 0.0429(8) | -0.1368(9) | 0.035(3) | 0.030(3) | 0.049(3) | 0.013(3) | 0.015(3) | -0.005(3) |
| C6 | 0.1512(2) | 0.4042(6) | -0.0727(6) | 0.019(2) | 0.021(2) | 0.025(2) | -0.001(2) | 0.003(2) | 0.003(2) |
| O6 | 0.1838(3) | 0.4954(8) | -0.1099(7) | 0.026(3) | 0.026(3) | 0.038(3) | -0.008(3) | 0.002(2) | 0.002(3) |
| C7 | 0.2450(2) | 0.2682(7) | 0.1851(4) | 0.014(2) | 0.035(3) | 0.022(2) | 0.002(2) | 0.002(1) | -0.006(3) |
| O7 | 0.2992(2) | 0.2769(9) | 0.1253(6) | 0.015(2) | 0.059(5) | 0.029(2) | -0.002(3) | 0.005(2) | 0.000(3) |
| C8 | 0.1836(2) | 0.2627(8) | 0.4944(4) | 0.019(1) | 0.036(2) | 0.020(2) | 0.002(2) | -0.001(1) | 0.002(3) |
| O8 | 0.2041(3) | 0.2694(11) | 0.6155(6) | 0.027(2) | 0.073(5) | 0.019(2) | -0.004(4) | -0.001(2) | 0.004(4) |
| C9 | 0.1575(3) | 0.0581(6) | 0.2748(7) | 0.022(2) | 0.026(3) | 0.033(3) | 0.002(2) | -0.005(2) | 0.004(2) |
| O9 | 0.1606(4) | -0.0552(7) | 0.2732(10) | 0.045(4) | 0.023(3) | 0.056(4) | 0.007(3) | -0.011(3) | -0.003(3) |
| C10 | 0.1374(3) | 0.4440(6) | 0.2675(6) | 0.023(2) | 0.024(3) | 0.020(2) | 0.003(2) | -0.002(2) | -0.000(2) |
| O10 | 0.1289(4) | 0.5537(7) | 0.2569(7) | 0.048(4) | 0.020(3) | 0.035(3) | 0.004(3) | -0.000(3) | -0.001(3) |
| C11 | 0.0264(2) | 0.0943(6) | 0.0649(5) | 0.021(2) | 0.014(2) | 0.025(2) | 0.003(2) | 0.002(2) | -0.002(2) |
| H1 | -0.0139(5) | 0.0568(11) | -0.0148(12) | 0.029(4) | 0.038(5) | 0.044(5) | -0.006(4) | -0.001(4) | -0.007(5) |
| H2 | 0.0501(5) | 0.0074(10) | 0.1194(11) | 0.033(4) | 0.022(4) | 0.042(5) | -0.003(4) | -0.002(4) | 0.007(4) |
| H3 | 0.0654(5) | 0.2233(10) | 0.3567(10) | 0.027(4) | 0.052(7) | 0.029(4) | -0.005(4) | 0.002(3) | 0.005(4) |
| H4 | 0.0336(5) | 0.3604(11) | 0.0755(13) | 0.032(4) | 0.027(4) | 0.047(6) | 0.012(4) | 0.009(4) | 0.004(5) |

$^a$ X, Y and Z are fractional coordinates. $^b$ Anisotropic temperature factors of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2a^*b^*U_{12}hk + \ldots)]$.

**Table III.** Principal Interatomic Distances (A) for
$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)$

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.824 (3) | Os(3)–C(8) | 1.941 (4) |
| Os(1)–Os(3) | 3.053 (3) | Os(3)–C(9) | 1.958 (7) |
| Os(2)–Os(3) | 2.855 (3) | Os(3)–C(10) | 1.966 (6) |
| Os(1)–H(3) | 1.883 (9) | C(1)–O(1) | 1.145 (6) |
| Os(3)–H(3) | 1.754 (8) | C(2)–O(2) | 1.131 (8) |
| Os(1)–H(4) | 1.834 (11) | C(3)–O(3) | 1.157 (8) |
| Os(2)–H(4) | 1.808 (10) | C(4)–O(4) | 1.130 (6) |
| Os(1)–C(11) | 2.151 (5) | C(5)–O(5) | 1.141 (8) |
| Os(2)–C(11) | 2.150 (6) | C(6)–O(6) | 1.148 (8) |
| Os(1)–C(1) | 1.891 (4) | C(7)–O(7) | 1.134 (6) |
| Os(1)–C(2) | 1.912 (6) | C(8)–O(8) | 1.129 (7) |
| Os(1)–C(3) | 1.949 (6) | C(9)–O(9) | 1.146 (8) |
| Os(2)–C(4) | 1.916 (4) | C(10)–O(10) | 1.122 (8) |
| Os(2)–C(5) | 1.903 (6) | C(11)–H(1) | 1.090 (11) |
| Os(2)–C(6) | 1.933 (6) | C(11)–H(2) | 1.091 (10) |
| Os(3)–C(7) | 1.927 (4) | | |

**Table IV.** Interatomic Angles (deg) for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)$

**(A) Angles about Os(1)**

| | | | |
|---|---|---|---|
| Os(2)–Os(1)–Os(3) | 57.96 (7) | H(3)–Os(1)–C(11) | 94.1 (3) |
| Os(2)–Os(1)–H(3) | 88.5 (3) | H(3)–Os(1)–C(1) | 172.4 (3) |
| Os(2)–Os(1)–H(4) | 38.8 (3) | H(3)–Os(1)–C(2) | 80.4 (3) |
| Os(2)–Os(1)–C(11) | 48.9 (1) | H(3)–Os(1)–C(3) | 86.8 (3) |
| Os(2)–Os(1)–C(1) | 98.3 (1) | H(4)–Os(1)–C(11) | 84.6 (3) |
| Os(2)–Os(1)–C(2) | 136.6 (2) | H(4)–Os(1)–C(1) | 85.5 (4) |
| Os(2)–Os(1)–C(3) | 125.0 (2) | H(4)–Os(1)–C(2) | 174.1 (4) |
| Os(3)–Os(1)–H(3) | 31.6 (3) | H(4)–Os(1)–C(3) | 89.2 (4) |
| Os(3)–Os(1)–H(4) | 72.7 (3) | C(11)–Os(1)–C(1) | 88.0 (2) |
| Os(3)–Os(1)–C(11) | 79.8 (2) | C(11)–Os(1)–C(2) | 89.9 (2) |
| Os(3)–Os(1)–C(1) | 155.8 (2) | C(11)–Os(1)–C(3) | 173.8 (2) |
| Os(3)–Os(1)–C(2) | 108.3 (2) | C(1)–Os(1)–C(2) | 92.3 (2) |
| Os(3)–Os(1)–C(3) | 98.0 (2) | C(1)–Os(1)–C(3) | 91.9 (2) |
| H(3)–Os(1)–H(4) | 102.0 (4) | C(2)–Os(1)–C(3) | 96.3 (2) |

**(B) Angles about Os(2)**

| | | | |
|---|---|---|---|
| Os(1)–Os(2)–Os(3) | 65.04 (8) | H(4)–Os(2)–C(11) | 85.2 (4) |
| Os(1)–Os(2)–H(4) | 39.5 (3) | H(4)–Os(2)–C(4) | 90.5 (4) |
| Os(1)–Os(2)–C(11) | 49.0 (1) | H(4)–Os(2)–C(5) | 172.7 (4) |
| Os(1)–Os(2)–C(4) | 103.2 (1) | H(4)–Os(2)–C(6) | 86.8 (4) |
| Os(1)–Os(2)–C(5) | 134.6 (2) | C(11)–Os(2)–C(4) | 89.6 (2) |
| Os(1)–Os(2)–C(6) | 122.6 (2) | C(11)–Os(2)–C(5) | 91.0 (2) |
| Os(3)–Os(2)–H(4) | 78.4 (4) | C(11)–Os(2)–C(6) | 171.6 (2) |
| Os(3)–Os(2)–C(11) | 84.6 (2) | C(4)–Os(2)–C(5) | 95.8 (2) |
| Os(3)–Os(2)–C(4) | 167.8 (2) | C(4)–Os(2)–C(6) | 93.2 (3) |
| Os(3)–Os(2)–C(5) | 95.0 (2) | C(5)–Os(2)–C(6) | 96.6 (2) |
| Os(3)–Os(2)–C(6) | 91.2 (2) | | |

**(C) Angles about Os(3)**

| | | | |
|---|---|---|---|
| Os(1)–Os(3)–Os(2) | 57.00 (7) | H(3)–Os(3)–C(7) | 173.4 (4) |
| Os(1)–Os(3)–H(3) | 34.3 (3) | H(3)–Os(3)–C(8) | 86.2 (3) |
| Os(1)–Os(3)–C(7) | 141.7 (2) | H(3)–Os(3)–C(9) | 84.0 (4) |
| Os(1)–Os(3)–C(8) | 118.8 (1) | H(3)–Os(3)–C(10) | 93.4 (4) |
| Os(1)–Os(3)–C(9) | 92.0 (2) | C(7)–Os(3)–C(8) | 98.9 (2) |
| Os(1)–Os(3)–C(10) | 81.6 (2) | C(7)–Os(3)–C(9) | 91.4 (3) |
| Os(2)–Os(3)–C(3) | 90.1 (3) | C(7)–Os(3)–C(10) | 90.5 (3) |
| Os(2)–Os(3)–C(7) | 85.0 (1) | C(8)–Os(3)–C(9) | 94.5 (3) |
| Os(2)–Os(3)–C(8) | 175.0 (2) | C(8)–Os(3)–C(10) | 93.0 (3) |
| Os(2)–Os(3)–C(9) | 88.4 (2) | C(9)–Os(3)–C(10) | 171.8 (2) |
| Os(2)–Os(3)–C(10) | 83.8 (2) | | |

**(D) Angles about Bridging Atoms**

| | | | |
|---|---|---|---|
| Os(1)–H(3)–Os(3) | 114.1 (5) | Os(1)–C(11)–H(2) | 116.4 (6) |
| Os(1)–H(4)–Os(2) | 101.7 (5) | Os(2)–C(11)–H(1) | 116.0 (6) |
| Os(1)–C(11)–Os(2) | 82.1 (2) | Os(2)–C(11)–H(2) | 119.7 (6) |
| Os(1)–C(11)–H(1) | 115.7 (6) | H(1)–C(11)–H(2) | 106.0 (8) |

**(E) Osmium–Carbon–Oxygen Angles**

| | | | |
|---|---|---|---|
| Os(1)–C(1)–O(1) | 177.6 (4) | Os(2)–C(6)–O(6) | 177.5 (6) |
| Os(1)–C(2)–O(2) | 175.7 (5) | Os(3)–C(7)–O(7) | 179.0 (5) |
| Os(1)–C(3)–O(3) | 173.3 (5) | Os(3)–C(8)–O(8) | 177.7 (4) |
| Os(2)–C(4)–O(4) | 178.5 (6) | Os(3)–C(9)–O(9) | 178.5 (7) |
| Os(2)–C(5)–O(5) | 177.8 (5) | Os(3)–C(10)–O(10) | 179.3 (6) |

The hydride atom which bridges Os(1)–Os(3) lies 0.286 (11) Å "above" the plane of the Os$_3$ triangle (see Figure 2), partially as a result of the tilting of the Os(1) and Os(3) coordination octahedra relative to the Os$_3$ plane; i.e., the carbonyls trans to H(3) lie "below" the Os$_3$ plane (see Table

**Table V**

Selected Planes$^a$ and Distances (Å) of Atoms from the Planes

**(A) Os(1)–Os(2)–Os(3) Plane**

$$0.0039X - 1.0000Y + 0.0086Z = 2.5084$$

| | | | |
|---|---|---|---|
| H(3) | 0.286 (11) | O(4) | −0.186 (12) |
| H(4) | −1.122 (10) | C(7) | −0.167 (8) |
| C(11) | 1.563 (5) | O(7) | −0.256 (11) |
| C(1) | −0.176 (8) | C(8) | −0.093 (9) |
| O(1) | −0.274 (10) | O(8) | −0.150 (14) |
| C(4) | −0.104 (9) | | |

**(B) Os(1)–C(11)–H(4) Plane**

$$0.8595X - 0.0602Y + 0.5076Z = -0.6512$$

| | | | |
|---|---|---|---|
| C(2) | −0.066 (12) | C(3) | 0.013 (7) |
| O(2) | −0.157 (18) | O(3) | −0.081 (10) |

**(C) Os(2)–C(11)–H(4) Plane**

$$0.5504X - 0.0561Y + 0.8330Z = -0.6892$$

| | | | |
|---|---|---|---|
| C(5) | −0.208 (13) | C(6) | −0.091 (8) |
| O(5) | −0.344 (21) | O(6) | −0.100 (10) |

**(D) C(11)–H(1)–H(2) Plane**

$$-0.6947X + 0.0436Y + 0.7180Z = -0.1106$$

| | | | |
|---|---|---|---|
| Os(1) | 1.469 (22) | C(9) | −0.381 (26) |
| Os(2) | −1.353 (23) | O(9) | −0.478 (28) |
| Os(3) | −0.176 (38) | C(10) | −0.001 (56) |
| H(4) | 0.088 (35) | O(10) | 0.088 (67) |

**Dihedral Angles, Deg**

| | | | |
|---|---|---|---|
| plane A–plane B | 86.1 (2) | plane B–plane C | 154.0 (5) |
| plane A–plane C | 93.7 (3) | plane B–plane D | 103.6 (5) |
| plane A–plane D | 92.2 (7) | plane C–plane D | 102.3 (6) |

$^a$ Equations of the planes are expressed in the orthonormal (Å) coordinate system: $X = xa$, $Y = yb$, and $Z = zc$.
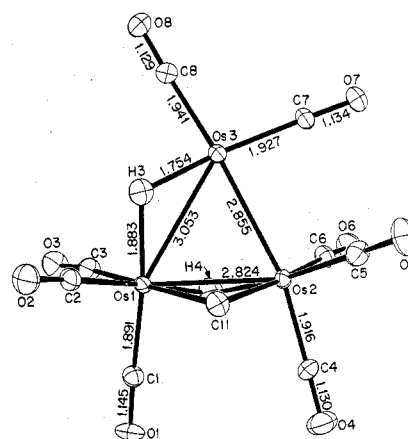


**Figure 2.** View of the plane of the three osmium atoms. The methylene hydrogen atoms and the mutually trans carbonyl ligands on Os(3) which point directly toward and away from the viewer have been omitted for clarity.

V). The Os(3)–H(3) distance of 1.754 (9) Å is 0.13 (1) Å shorter than the Os(1)–H(3) distance of 1.883 (9) Å, which is an indication of the chemical nonequivalence of Os(1) and Os(3). A contrasting situation is observed for H(4) (see Figure 3), for which the Os(1)–H(4) and Os(2)–H(4) distances of 1.834 (11) and 1.808 (10) Å, respectively, differ by only 2.5$\sigma$ and are bracketed by the two Os–H(3) bond lengths, although Os(1) and Os(2) are also chemically nonequivalent. By comparison, the average bridging Os–H distance in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ is 1.845 (3) Å and the average terminal Os–H distance in $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ is 1.659 (3) Å.[18] Because of the short Os(1)–Os(2) distance relative to the Os(1)–Os(3) distance, the Os(1)–H(4)–Os(2) angle of 101.7 (5)° is 12.4 (7)° less than the Os(1)–H(3)–Os(3) angle of 114.1 (5)°. The dihedral angle between the Os(1)–Os(2)–H(4) plane and the

**Table VI.** Comparison of the Structural Geometries of Compounds with Bridging Methylene or Substituted-Methylene Ligands

| compd | M–M, Å | M–C,[a] Å | M–C–M, deg | H–C–R,[b] deg | ref |
|---|---|---|---|---|---|
| $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ | 2.824 (3) | 2.150 (4) | 82.1 (2) | 106.0 (8) | this study[c] |
| $[\eta^5\text{-}C_5H_5)Rh(CO)]_2(\mu\text{-CH}_2)$ | 2.6649 (4) | 2.04 (1) | 81.7 (1) | d | 7[e] |
| $[Ru(PMe_3)_3]_2(\mu\text{-CH}_2)_3$ | 2.650 (1) | 2.108 (5) | 78.0[f] | g | 8[e] |
| $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$ | 2.8002 (6) | 2.16 (1) | 80.8 (3) | 113 (4) | 16[e] |

[a] The esd's are the largest of two values calculated by $\sigma(\bar{x}) = [\Sigma_m \sigma_i^2/m^2]^{1/2}$ and $\sigma(\bar{x}) = [\Sigma_m(x_i - \bar{x})^2/m(m-1)]^{1/2}$, where $\bar{x}$ is the mean value. [b] R = H or $CHCH_2PMe_2Ph$. [c] Neutron diffraction study. [d] See the added note in ref 7. [e] X-ray diffraction study. [f] The esd was not given in ref 8. [g] The H–C–H angles were not given in ref 8.
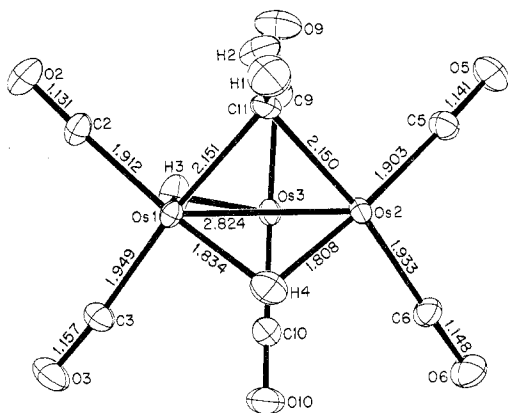


**Figure 3.** View of the doubly bridged edge of the triosmium triangle. Carbonyl ligands 1, 4, 7, and 8 (see Figure 2) have been omitted for clarity.

$Os_3$ plane is 102.5 (6)°, which differs by 3.0 (6)° from the dihedral angle between the Os(1)–Os(2)–C(11) and the $Os_3$ planes of 105.5 (2)°.

Although metal–carbene complexes have been proposed as intermediates in many catalytic reaction sequences,[6] there are only three other structural reports (all X-ray diffraction studies) of stable compounds which contain a methylene ligand. The first is the monomeric tantalum complex Ta($\eta^5$-$C_5H_5)_2(CH_3)(CH_2)$, which has a Ta–C bond distance of 2.026 (10) Å and an H–C–H angle of 107 (9)°.[19] The other two structures[7,8] contain bridging methylene ligands, and a comparison of their geometries with $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ is presented in Table VI. In addition, because of the remarkable similarity between the geometries of the bridging carbon atoms of the methylene in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ and of the dipolar species $C^-HCH_2P^+Me_2Ph$ in $(\mu\text{-H})Os_3$-$(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$,[16] the latter compound is also included in Table VI. This similarity indicates that, although $C^-HCH_2P^+Me_2Ph$ is formally a three-electron donor, upon coordination the bridging carbon atom adopts the same electronic, and therefore molecular, structure as the two-electron-donating $CH_2$ species (vide infra).

The spatial arrangements of the atoms around the coordinated methylene carbon atoms presented in Table VI are best characterized as distorted tetrahedral. In $(\mu\text{-H})_2Os_3$-$(CO)_{10}(\mu\text{-CH}_2)$, the dihedral angle between the Os(1)–Os(2)–C(11) and C(11)–H(1)–H(2) planes is 88.8 (4)° and three of the four Os–C(11)–H angles have an average value of 116.0 (3)° with an anomalous angle of 119.7 (6)° for Os(2)–C(11)–H(2). The M–C–M angles of three of the complexes in Table VI are nearly equal with an average value of 81.5°. Apparently, the Ru–C–Ru angle is 78.0° in the tribridged Ru dimer because of the short Ru–Ru distance and the long Ru–C distance of 2.108 (5) Å relative to 2.04 (1) Å in the Rh dimer. The two H–C–R angles of 106.0 (8) and 113 (4)° given in Table VI imply $sp^3$ hybridization for the carbon atom. However, the terminally bonded $CH_2$ in Ta-($\eta^5$-$C_5H_5)_2(CH_3)(CH_2)$ is clearly $sp^2$ hybridized but has an H–C–H angle of 107 (9)°.[19] Thus, we must stress that the H–C–H angle is *not* a reliable indication of the methylene

**Chart I**
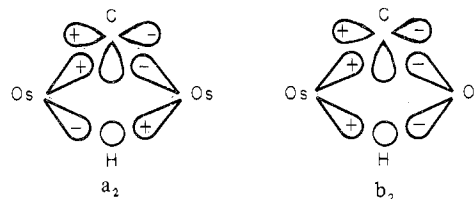


carbon hybridization state. The two Os–C(11) bond distances in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ are equal (2.151 (5) and 2.150 (6) Å) and are virtually equivalent to the average Os–($\mu$-C) distance of 2.161 (1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$. As seen in Figure 3, H(4) and Os(3) deviate only 0.09 (4) and 0.18 (14) Å, respectively, from the C(11)–H(1)–H(2) plane, which has dihedral angles of 92.2 (7) and 88.8 (4)° with the $Os_3$ and Os(1)–Os(2)–C(11) planes, respectively.

For each of the three Os atoms in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$, the carbonyl ligands trans to the hydrides have the shortest Os–C distances. This negative trans influence,[20] which is characterized by a relatively short metal–ligand distance trans to a hydride, in this case, is also observed in $(\mu\text{-H})_2Os_3(CO)_{10}^2$ and is generally true for other metal–hydride compounds with respect to carbonyl ligands.[21] By comparison, the Os(2)–Os(3) bond has a positive trans effect on the trans carbonyl ligands, and, as expected, the mutually trans carbonyl ligands on Os(3) exhibit the longest Os–C bond distances. Of most interest is the positive trans influence of the bridging $CH_2$ ligand, such that the longest Os–CO distances for Os(1) and Os(2) are for the carbonyl ligands trans to $CH_2$. Thus, the formally electron-deficient carbene may also be an electron acceptor (vide infra) with a destabilizing effect on the trans Os–CO bond.

These structural observations are readily accounted for by the qualitative molecular orbital scheme presented in the preceding paper for $(\mu\text{-H})_2Os_3(CO)_{10}$.[2] In $(\mu\text{-H})_2Os_3$-$(CO)_{10}(\mu\text{-CH}_2)$, there are eight electrons from each Os atom, two from each CO, one from each hydride, and two from the methylene ligand for a total of 48 electrons. With six electrons from each Os atom in nonbonding $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals, the remaining metal orbitals form $sp^3d^2$ hybrids. Twenty electrons are involved in Os–CO bonding, the Os(2)–Os(3) bond uses two electrons, and the Os(1)–H(3)–Os(3) interaction is considered a three-center, two-electron bond. Furthermore, if we consider the methylene carbon atom to be $sp^2$ hybridized,[22] linear combinations of four $sp^3d^2$ orbitals from Os(1) and Os(2), the 1s orbital from H(4), and the C(11) $sp^2$ orbital produce the same six molecular orbitals depicted for $(\mu\text{-}H)_2Os_3(CO)_{10}$, for which four electrons are required to fill the $a_1$ and $b_1$ bonding orbitals.

This accounts for 46 electrons, which is the total for $(\mu\text{-}H)_2Os_3(CO)_{10}$, but leaves two electrons unaccounted for in the 48-electron system of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$. As shown in Chart I, the methylene carbon atom has an unfilled $p\pi$ orbital with the correct symmetry to form a bonding interaction with the $a_2$ or $b_2$ MO. Filling one of these orbitals with two electrons accounts for all 48 electrons, produces a six-

electron, four-center $Os_2(\mu\text{-H})(\mu\text{-C})$ bond, and explains the observation of a positive trans influence for the $CH_2$ ligand (vide ante). Furthermore, since the $a_2$ and $b_2$ MO's are metal–metal antibonding, the model predicts the six-electron, four-center bond has a metal–metal bond order of 1, and removal of two electrons leads to a metal–metal double bond. The observed doubly bridged Os–Os distances of 2.824 (3) and 2.683 (1) Å in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ and $(\mu\text{-H})_2Os_3\text{-}$ $(CO)_{10}$,[2] respectively, agree with the model. In addition, the $Os(1)\text{-}Os(2)$ bond length is within the range of the nonbridged Os–Os single-bond distances of 2.814 (1) and 2.815 (1) Å in $(\mu\text{-H})_2Os_3(CO)_{10}$ and 2.855 (2) Å in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}$ $CH_2)$.

This bonding scheme can be extended to other 48-electron triosmium and triruthenium systems. Since the $C^-HCH_2P^+Me_2Ph$ ligand is a three-electron donor, $(\mu\text{-H})\text{-}$ $Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$ is a 48-electron system with only one hydride, and it can adopt a four-center, six-electron $Os_3(\mu\text{-H})(\mu\text{-C})$ bond using the bridging carbon $p\pi$ orbital. In $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-C}\!=\!NMe_2)$,[23] the $C^-\!=\!N^+Me_2$ ligand is also a three-electron donor and the $M_2(C\!=\!NC_2)$ moiety is nearly planar such that the $C\text{-}NMe_2$ $\pi$ bond is oriented perpendicular to the plane. If the $\mu\text{-C}$ atom is assumed to be sp hybridized, then the remaining $p\pi$ orbital lies in the molecular plane and it can therefore successfully interact with the $a_2$ and $b_2$ MO's. However, as previously discussed,[2] the addition of various other two-electron donor ligands to $(\mu\text{-}$ $H)_2Os_3(CO)_{10}$ yields a molecule with one bridging hydride as the only bridging ligand, as in $(\mu\text{-H})HOs_3(CO)_{11}$[24] and $(\mu\text{-}$ $H)HOs_3(CO)_{10}(PPh_3)$.[25] These observations can be rationalized if the $\pi^*$ and $\pi$ orbitals for $CO$[26] and $PPh_3$, respectively, cannot form a stable interaction with the $a_2$ and $b_2$ orbitals. Therefore, since these orbitals are metal–metal antibonding, the molecule adopts the $(\mu\text{-H})HOs_3(CO)_{10}L$ (L = terminal CO or $PPh_3$) structural form.[2]

The structure of 48-electron triiron systems is also consistent with this bonding model but without the qualification with respect to carbonyl ligands.[27] The most obvious example is $Fe_3(CO)_{12}$,[28] which has two CO ligands symmetrically bridging two Fe atoms, whereas $Ru_3(CO)_{12}$[29] and $Os_3(CO)_{12}$[30] contain only terminally bonded carbonyls. Furthermore, the structure of $HFe_3(CO)_{11}^-$ has a hydride and a carbonyl bridging two Fe atoms.[31]

It would be extremely satisfying if we could conclude at this point that, based on our bonding scheme, the methyl tautomer $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ is a 46-electron system and should have a structure analogous to $(\mu\text{-H})_2Os_3(CO)_{10}$. This is not the case, since recent NMR evidence indicates the existence of a three-center, two-electron C–H–Os interaction.[32] Thus, it is possible to consider the methyl tautomer as a 48-electron system with six electrons involved in the $Os_2(\mu\text{-H})(\mu\text{-CH}_3)$ moiety. An analogous case is that of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}$ $CH\!=\!CH_2)$, in which the vinyl ligand $\sigma$ bonds to one Os atom and $\pi$ bonds to a second Os atom, which are also bridged by a hydride, as established by NMR evidence.[33] However, the structures of many $Os_3(CO)_{10}(alkyne)$ complexes are further complicated by triply bridging ligands and semibridging carbonyls,[34] which cannot be easily described in terms of the bonding scheme presented here.

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